DOI 10.1007/s10717-014-9641-y
Glass and Ceramics, Vol. 71, Nos. 5 – 6, September, 2014 (Russian Original, Nos. 5 – 6, May – June, 2014)

UDC 691.618.93

DIATOMITES IN GRANULAR FOAM-GLASS TECHNOLOGY

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Translated from *Steklo i Keramika*, No. 5, pp. 15 – 19, May, 2014.

The present status of research on the production of foam-glass from siliceous rock by the one-step scheme is examined. The main technological principles of the experimental production of granular foam-glass based on diatomites are formulated. The production process is described and the main properties of the 5 – 10 mm fraction as compared with the normative requirements are presented.

Key words: siliceous rocks, diatomite, diatomaceous foam-glass, liquid glass.

The simplification and cost reduction of the technology of granular foam-glass, which is an environmentally clean material in high demand, are problems of current interest [1 – 5]. The trends in this field consist of the following.

The process of obtaining foam-glass in the form of granules is the most easily implementable technology for producing foam-glass in the form of a building product ready for use.

In the heat-treatment process the cross section of a granule is subject to smaller temperature gradients than foam-glass blocks, which simplifies the foaming and annealing processes. A tunnel furnace many meters long and a stock of special molds are not required.

Granular foam-glass has a wide range of applications, starting from heat-insulation fills and fillers in light concretes to thermal stabilization of the foundations of engineered structures. It is especially important to obtain fine granular foam-glass for developing new materials in order to impart special properties to them.

Alternative forms of mineral raw materials of natural and technogenic origin can be used in production [1 – 4].

All together this can lead to the development of higher-quality materials and inexpensive modern products. For example, the use of siliceous rocks and NaOH in batch makes it possible to obtain granular foam-glass without intermediate glassmaking or the use of cullet, i.e., in one step, which greatly simplifies production [2 – 4]. However, even though this method is promising its practical mastery is still in the R&D stage.

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In this connection our research has been concerned with the development of granular foam-glass technology using widely available diatomites as raw material. This work was financed by the Committee on Innovations as part of a state-supported program in the sphere of scientific, scientific-engineering and innovational work in Tyumen Oblast’. The objective of this work was to develop experimental mini-production on the basis of the Institute of the Earth’s Cryosphere at the Siberian Branch of the Russian Academy of Sciences.

Significant reserves of siliceous or cristobalite-opaline rocks (diatomite, trepel, opoka) of the Upper Cretaceous and Paleogene are located in the northern part of Tyumen Oblast’. A 1000 km long and up to 100 km wide band of rock outcroppings forming the North-Tyumenskaya subprovince of siliceous rocks encompasses the Khanty-Mansiiskii and Yamalo-Nenetskii Autonomous Districts [6, 7]. The predicted geological reserves of siliceous rocks within the province (to depth 10 m) reach 0.3×10^{12} m^3, but on the whole the North-Tyumenskaya subprovince has no equals in Russia in terms of reserves [6].

Diatomite from the Irbitskoe deposit in Sverdlovsk Oblast’ was used in the present work. The chemical composition of the rock fluctuates in the following range (wt.%): SiO_2 7.94 – 84.7; CaO 0.1 – 1.5; MgO 0.7 – 1.5; Al_2O_3 4.3 – 10.3; Fe_2O_3 3.6 – 5.3; TiO_2 0.4 – 0.7; $Na_2O + K_2O$ 0.7 – 1.2; SO_3 0.2 – 1.3; losses to calcination 6.5 – 8.0. Specimens of diatomite from the Novo-Urengoiskoe deposit in Tyumen Oblast’ (Yamalo-Nenetskii Autonomous District) had a similar chemical composition, and the properties of the foam-glass specimens based on it, which were obtained in the course of preliminary research, were at least as good as those of the samples based on Irbistkoe diatomite. This confirms that the rocks from the two subprovinces — Zaural’skaya

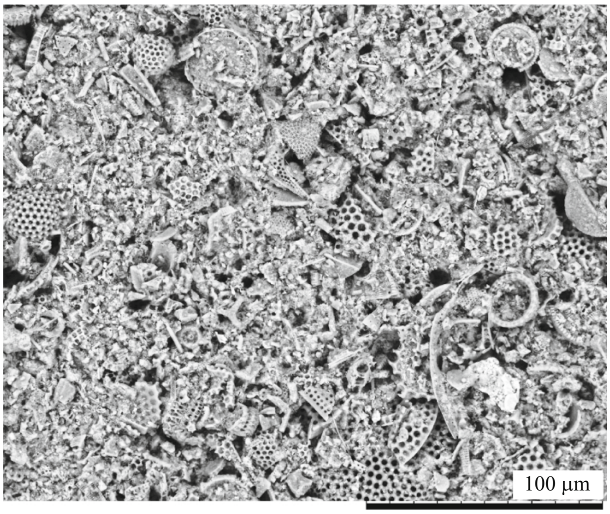

Fig. 1. Diatomite from the Irbitskoe deposit.

and Severo-Tyumenskaya — belong to the same geological formation and have chemical and mineralogical affinity [6].

It is clearly seen in Fig. 1 that a diatomite is comprised mainly of shells of diatoms, fossils of algae, consisting of amorphous SiO_2. X-ray phase analysis of a specimen of Irbitskoe diatomite shows an amorphous component in the form of opal; the crystalline phase consists of β-quartz, hydromica and feldspar. The chemical and phase compositions of the rock correspond to the data presented in [9].

The reactivity of siliceous rocks is determined by the content of amorphous (opaline) SiO_2. Hydrothermal treatment of the rocks with a solution of NaOH promotes leaching, i.e., a transition of SiO_2 into a soluble state with formation of liquid glass. For Irbitskoe diatomite the experimentally determined amount of dissolved SiO_2 reaches 45% of the mass of the initial specimen. The result obtained agrees well with the data in [10].

The replacement of NaOH with an equivalent amount of soda ash in order to reduce the materials cost does not give significant SiO_2 yield. For the time being this makes it possible to use the latter either in two-step technology [11] or in autoclave leaching of siliceous rock.

The analysis performed shows Irbitskoe and Novo-Urengoiskoe diatomites to be promising initial materials with the requisite reactivity for obtaining diatomaceous foam-glass by the one-step technology using NaOH.

The existing studies on obtaining foam-glass materials based on siliceous rocks essentially reduce to adjusting the chemical composition of batch, corresponding to perlite or conventional foam-glass [8]. For this a solution of NaOH or KOH, which creates a gel-like gas-permeable phase (liquid glass) in the mixture, is introduced into powder comprised of comminuted siliceous rock. Heating such mixtures consisting essentially of liquid glass, an almost insoluble crystalline component of rock (quartz, clay minerals, feldspar and so on) and organic impurities can cause foaming with the formation of a cellular glass mass in the single-step scheme.

Current studies in this field also note preliminary synthesis of liquid glass during the interaction of the amorphous component of siliceous rocks with alkalis [2 – 4].

We shall examine the data on the transformations of alkali-silicate compositions in order to validate the choice of technological process.

The foaming of liquid glasses at 300 – 600°C is well known and is used to obtain so-called heaters of hot foaming [12]. The formation of cellular materials is accompanied by the removal of molecular and silanol water followed by polycondensation of silicon-oxygen anions. Subsequent heating results in the formation of structures close to the corresponding glasses obtained from melt [13].

Heating drops of liquid glass with the molar ratio $Na_2O : SiO_2 = 1 : 3$ up to 750°C results in a structure consisting of hollow bubbles [14]. In addition, β-$Na_2Si_2O_5$ forms (in the range 400 – 700°C), transforming at 750°C into $Na_6Si_8O_{19}$, and after the temperature increases to 800°C or higher a melt appears, as a result of which the material becomes amorphous.

Heating mixtures of siliceous rock and NaOH in the temperature interval 200 – 800°C also results in foaming and is accompanied by a density reduction of the specimens [15]. The density starts to increase at temperatures 800°C and higher.

The density or foaming ratio of the compositions studied depends directly on the amount of SiO_2 extracted by leaching with formation of hydrated alkaline silicates. For example, hydrothermal leaching of opoka at 90°C increases the content of dissolved SiO_2, which intensifies pore formation and results in a density reduction of the specimens foamed at 850°C as compared with the samples without hydrothermal treatment [15].

A similar trend is observed in studies where a change in the leaching regime with the same NaOH content in the batch halves the density of the foamed specimens of diatomaceous foam-glass.

The following conclusions can be drawn from an analysis of the data presented.

1. The foaming of the initial compositions occurs as a result of the formation of liquid glass in the charge. In addition, the formation of a cellular structure precedes the formation of melt and the transition into the pyroplastic state.

2. For the same ratio of siliceous rock and NaOH in the initial batch the structure of the material will be determined by the content of dissolved SiO_2, which depends on the conditions of leaching.

As a rule the mass ratio of the siliceous rock and NaOH conventionally introduced into the batch lies in the range 5 – 7 [2 – 4]. This ratio was taken to be 7 on the basis of economic considerations.

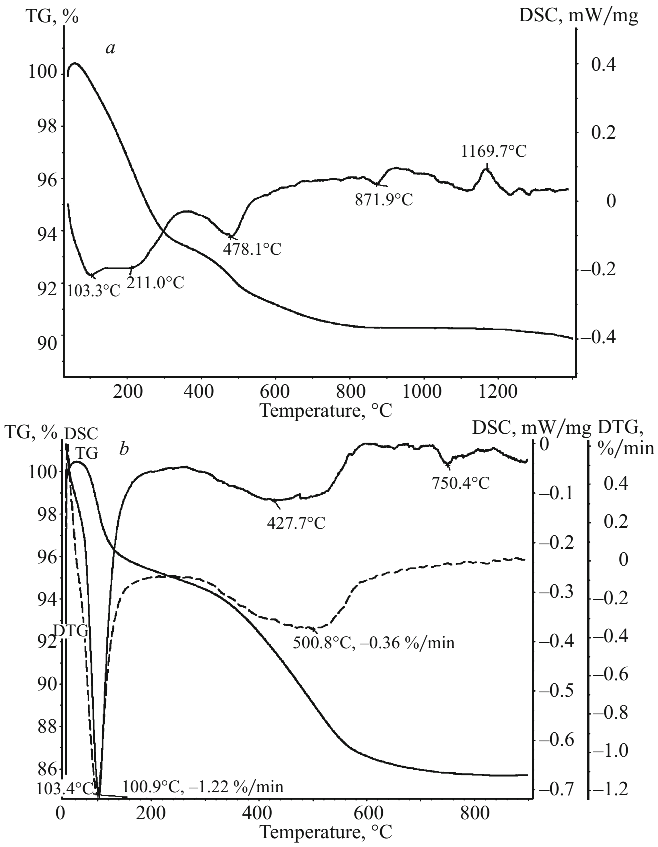

Fig. 2. The results of a thermal analysis of Irbitskoe diatomite (*a*) and its mixture with NaOH (*b*).

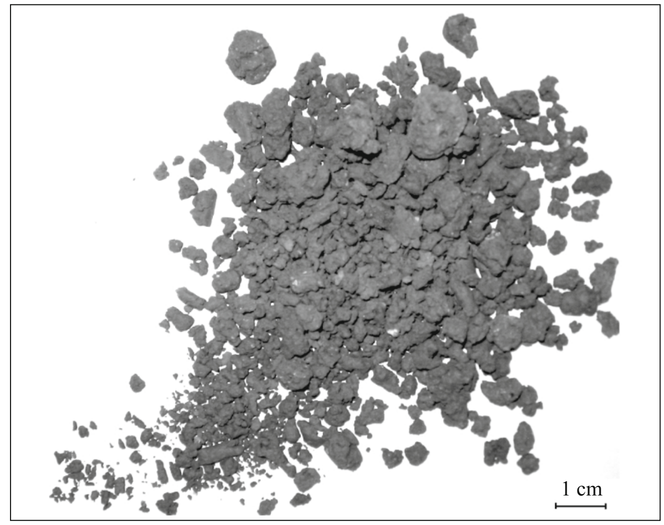

Fig. 3. Mixture of diatomite and NaOH after heat-treatment and comminution.

The results of a thermal analysis of a specimen of Irbitskoe diatomite and its mixture with NaOH in the adopted ratio are presented in Fig. 2.

Continual heating of rock results in stepped mass loss (Fig. 2*a*, TG curve). About 80% of the total losses associated with the removal of adsorption water and burnup of organic impurities occur below 400°C. Diatomite from the Inzenskoe deposit in Ul'yanovsk Oblast' undergoes similar mass changes on heating [17].

The mass change occurring when a mixture of diatomite with NaOH is heated is of a different character. The main losses occur in a higher temperature range: 150 – 630°C (Fig. 2*b*). This shift confirms the formation of hydrated alkaline silicates in the mixture and is associated mainly with their dehydration.

It follows on this basis that the technology of the production of foam-glass materials by the one-step scheme should ensure, first and foremost, the best conditions for silicate formation reactions. From our point of view the following requirements best correspond with this:

– calcination of siliceous rock at 300 – 600°C followed by fine comminution in order to increase their reactivity;

– introduction of sodium hydroxide in the form of a water solution with temperature no higher than 30°C into the batch; higher temperatures result in rapid formation of lumps and impedes the subsequent processing of the batch;

– intense forced mixing of the batch followed by hydrothermal processing.

These basic principles formed the foundation of the experimental production process that we developed. We shall now examine the main steps.

The primary comminution of diatomite occurs in a twin-shaft clay ripper followed by stone separation. Next, pieces of rock up to 20 mm in size are fed into a rotary furnace for drying and calcination at 500°C. Fine comminution of rock occurs in a batch-loading ball mill.

The diatomite pulverized into powder and the NaOH solution are continually fed in appropriate proportions into a screw-conveyor mixer, which mixes the components, compacts the mixture and extrudes it through prescribed openings. The extrusion method of combining components promotes maximum homogenization and primary heating of the batch as well as granulation giving 10 mm in diameter particles up to 30 mm long.

The raw granules formed in this manner are subjected to heat treatment in a rotary-drum furnace. The granules entering the furnace are treated with water vapor according to the counterflow principle. Moving along the drum the granules enter a zone with temperature 400 – 500°C. Intense vaporization occurs here, accompanied by partial dehydration and solidification of the granules as a result of polycondensation of silicon-oxygen anions of alkali silicates. After thermal preparation the intermediate product is comminuted in a mill in order to impart the required granulometric composition to the finished product (Fig. 3).

The granules foam up in the drum furnace with an external electric heater. The furnace is divided into a zone where granules are heated to 650°C and a zone of foaming at 790 – 850°C. The capacity of the furnace reaches 200 li-

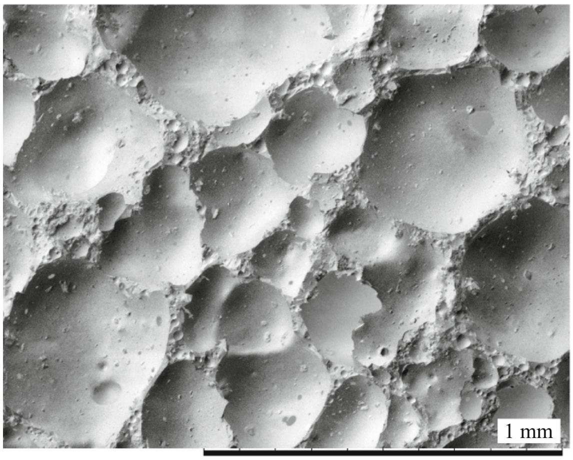

Fig. 4. Foamed granules.

TABLE 1. Main Properties of Granular Diatomaceous Foam-Glass

Index	Result	Normative specifications	
		TU 5914-001-15068529–2006	TU 5914-001-73893595–2005
Bulk density, kg/m^3	280	250 ± 50	251 – 300
Strength in compression, MPa	1.4	≥ 0.7	0.6 – 0.8
Thermal conductivity in charge, W/(m · K)	0.070	≤ 0.075	≤ 0.073
Frost resistance,* %	1.1	≤ 5	≤ 8
Water absorption by volume, %	3.4	–	2 – 20
Resistance to silicate decomposition, %	0.2	≤ 3	≤ 5

* Mass loss of material after 15 freeze-thaw cycles.

ters/h with a 3 m long drum and power consumption in the working regime 14 kW.

Owing to the partial softening in the drum furnace the foamed granules have a rolled form unlike the initial crushed intermediate product (Figs. 4 and 3, respectively). The fine-milled refractory powdering agent, which is sieved out after the furnace and is recycled, prevents the granules from sticking to one another.

The main properties of the product obtained in the form of a 5 – 10 fraction in comparison with the operating normative specifications are presented in Table 1.

The proposed technology makes it possible to obtain fine-granular foam-glass: the content (by weight) of the 0.14 – 2.5 mm sand fraction with bulk density about 350 kg/m^3 can reach half the total volume of the granules produced.

The cellular structure of diatomaceous foam-glass has a characteristic glassy luster. The closed pores fluctuate in size from several microns to several millimeters. An enlarged image of a cleavage face of a granule (Fig. 4) shows that the entire volume of the initial silicate mixture foams up because of the method picked to prepare it.

The experimental production makes it possible to produce diatomaceous foam-glass in the volumes required for full-scale tests under real conditions:

– filling of the experimental sections of the foundations of engineered structures (roads, buildings, pipelines and so on) in the Far North for thermal stabilization (protection from frost heaving and thermokarst);

– construction of a series of low buildings using the product at different stages of the work: in pouring a continuous foundation, raising block and monolithic walls, building bridges, monolithic floor ties and coverings and heat-insulation fills (including for heat-insulation of underground parts of buildings).

Organizing the proposed technology in Yamalo-Nenetskii Autonomous District of Tyumen Oblast' will make it possible to reduce production costs considerably by obtaining raw materials from the many nearby deposits, using inexpensive casing-head gas from gas fields and obtaining cheaper electricity from numerous state regional electric power plants located in the region. This solves the problem of supplying the region with heat-insulation materials that are in high demand.

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